

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 July 2001 (05.07.2001)

PCT

(10) International Publication Number
WO 01/47870 A2

(51) International Patent Classification⁷: C07C 269/04,
271/28

PO Box 155, Thane Belapur Road, Thane, Maharashtra
400601 (IN). SAPRE, Nitin, Yashwant [IN/IN]; ICI India
R & T Centre, Thane Works. PO Box 155, Thane Belapur
Road, Thane, Maharashtra 400601 (IN). BOSMAN, Joris
[BE/BE]; Wezelsbaantje 29B, B-2230 Herselt (BE).

(21) International Application Number: PCT/EP00/12889

(22) International Filing Date:
18 December 2000 (18.12.2000)

(74) Agents: MOENS, Marnix, Karel, Christiane et al.; In-
tellectual Property Dept., Everslaan 45, B-3078 Everberg
(BE).

(25) Filing Language: English

(26) Publication Language: English

(81) Designated States (*national*): IN, US.

(30) Priority Data:
961/BOM/99 27 December 1999 (27.12.1999) IN

(84) Designated States (*regional*): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).

(71) Applicant (*for all designated States except US*): HUNTS-
MAN ICI CHEMICALS, LLC [US/US]; 500 Huntsman
Way, Salt Lake City, UT 84108 (US).

Published:

— Without international search report and to be republished
upon receipt of that report.

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): MANDAL, Sisir,
Kumar [IN/IN]; ICI India R & T Centre, Thane works,

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*



WO 01/47870 A2

(54) Title: PROCESS FOR THE PRODUCTION OF AROMATIC POLYCARBAMATES

(57) Abstract: A process for the preparation of an aromatic polycarbamate which comprises reacting an aromatic polyamine, urea and an alcohol, characterised in that the alcohol is an alkoxyated monoalcohol.

PROCESS FOR THE PRODUCTION OF AROMATIC POLYCARBAMATESDESCRIPTION

- 5 The present invention relates to a process for the production of aromatic polycarbamates from aromatic polyamines, urea and an alcohol.

Processes for preparing carbamates by reacting amines with urea in the presence of an alcohol have been described in the art.

10

- In US-A 2.677.698 a process is described for the preparation of N-monosubstituted carbamic acid esters which comprises reacting a primary amine with urea to prepare a 1,3-disubstituted urea which is separated from unreacted amine, urea and generated ammonia and then reacted in a second step with a mono-hydroxy alcohol to give the resultant N-monosubstituted carbamic acid ester.

- US-A 2.409.712 concerning the pyrolysis of N-alkyl carbamic alkyl esters discloses a method for the preparation of such carbamic esters by reacting urea, an amine such as laurylamine or beta (isobutoxymethoxy)ethylamine and alcohols such as ethoxyethoxyethanol to give the N-alkyl carbamic alkyl esters.

- In EP-A 18.586 aliphatic, cycloaliphatic, arylaliphatic and aliphatic-cycloaliphatic N-substituted di- and polyurethanes are prepared by reacting primary aliphatic, cycloaliphatic, arylaliphatic or aliphatic-cycloaliphatic di- or polyamines with urea and alcohol. The yield obtained when converting hexanediamine to the corresponding carbamate using butanol or octanol was at least as high as when using 2-butoxyethanol.

- In EP-A 18.588 the N-unsubstituted carbamate based on 2-butoxyethanol was used to make a carbamate from hexanediamine. The use of the N-unsubstituted carbamates of butanol or octanol resulted in slightly higher yields.

- EP-A 27.940 discloses the conversion of aniline and 4-methoxyaniline to the corresponding carbamate using 2-butoxyethanol in the presence of a catalyst.

40

US-A 5.453.536 discloses the pyrolysis of polycarbamates into polyisocyanates and secondary alcohols.

While these processes have their advantages, there is a continuous need
5 for a simple, economical process for preparing aromatic polycarbamates via this route.

According to the present invention there is thus provided an alternative process for the preparation of aromatic polycarbamates which comprises
10 reacting an aromatic polyamine with urea and an alkoxyated monoalcohol, with high yields of aromatic polycarbamates and high conversion rates of the reactants and short reaction times, even in the absence of a solvent and/or catalyst.

The invention thus concerns a process for the production of aromatic polycarbamates by reaction of aromatic polyamines with urea and an alcohol, characterised in that the alcohol is an alkoxyated monoalcohol.

Preferably, the alkoxyated monoalcohol used has the structure $\text{HO}-\text{CHR}^1(\text{CR}^2\text{R}^3-\text{O})_x\text{R}^4$ wherein x is an integer between 1 and 250 and $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ each are independently H or hydrocarbon radicals.

The term 'polyamines' as used herein refers to compounds having more than 1 amine group.

Suitable aromatic polyamines include, for example, 3,3'-dimethyl-4,4'-diphenyldiamine, phenylenediamines, 2,4'- and 4,4'-methylenedianiline, sulfonyldianilines, thiodianilines, diaminodiphenylmethanes and higher homologs polyaminopolyphenylmethanes, toluediamines, m-phenylene diamine, 1,5-naphthylenediamine and the like, and mixtures thereof.

Preferred are aromatic diamines or higher functionality polyamines like toluediamines, diaminodiphenylmethanes or polyaminopolyphenylmethanes or any mixtures thereof.

Any mixtures of aromatic dicarbamates and higher functionality polycarbamates may be obtained depending on the composition of the starting amine compound.

Although any alkoxyated monoalcohol of the abovementioned structure can be used in the present process, the group of alcohols according to the above formula wherein $x=1$ have proven particularly useful.

Alcohols which are thus preferably employed in at least stoichiometric amounts based on the aromatic primary amine are, for example, 2-methoxyethanol, 2-ethoxyethanol, 2-ethoxycyclopropanol, 2-isopropoxyethanol, 1-methoxy-2-propanol, 2-methoxy-3-propanol, 2-methoxy n- and iso-butyl alcohols, 2-methoxy amyl alcohol, 2-methoxyhexanol, 2-methoxy heptanol, 2-methoxyoctanol, 2-methoxy nonanol, 2-methoxydecanol, 2-methoxy 2-ethyl hexanol, 2-methoxy 2-methyl pentanol, 2-methoxy 2-ethyl-1-butanol, 2-methoxy 3,5-dimethyl-1-hexanol, and the like.

Particularly preferred alcohols are 2-methoxyethanol, 2-ethoxyethanol, 2-isopropoxyethanol, 1-methoxy-2-propanol, or mixtures thereof.

Although small amounts of a catalyst, i.e. between about 0.1 to 5.0 mole percent, based on the aromatic polyamine may be added to the reaction mixture if desired, it was found that even in the absence of a catalyst high yields of aromatic carbamates were obtained. A catalyst-free process is thus preferred.

Although the process of the invention is preferably carried out using the alkoxyalcohol as the reaction solvent, as well as reactant, other solvents or mixtures of solvents which are stable and substantially chemically inert to the components of the reaction system may be employed as a co-solvent in the reaction system if desired. Suitable inert solvents which may be employed, and generally in amounts of up to 50 weight percent based on the reaction mixture, include, for example, aromatic hydrocarbons such as benzene, halogenated aromatic hydrocarbons such as monochlorobenzene, ortho-dichlorobenzene or 1-chloronaphthalene, alkylated aromatic hydrocarbons like toluene, xylene, ethylbenzene, cumene or tetrahydronaphthalene, other functionalised aromatic hydrocarbons such as anisol, diphenylether, ethoxybenzene, benzonitrile, 2-fluoroanisole, 2,3-dimethylanisole or trifluorotoluene, alkanes such as n-pentane, n-hexane, n-heptane or higher or branched alkanes, cyclic alkanes like cyclopentane, cyclohexane or derivatives thereof, halogenated alkanes like chloroform, dichloromethane, carbontetrachloride, and alkanes with other functional groups like diethylether, acetonitrile, dioxane or

mixtures thereof, and the like

Examples of preferred solvents are halogenated aromatic hydrocarbons. Particularly preferred are monochlorobenzene and ortho-dichlorobenzene.

The ratio of reactants may be varied over any convenient range. In general, the mole ratio of amine to urea may be between about 1:1 to 1:20, preferably between about 1:1.2 to 1:10, and more preferably between about 1:1.2 and 1:5. It is generally more convenient and preferred to employ the reactant alcohol as reaction solvent and thus in excess of the stoichiometric quantity required for the reaction. Amounts of up to 50 molar excess based on the amine employed may be conveniently employed.

The reaction conditions largely depend on the type of reactants used, but are chosen so that substantially all of the amines are converted into the corresponding carbamates.

The reaction of the present invention will proceed at temperatures of from about 100 to 250°C. It is generally preferred to operate the process at temperatures of from about 150 to 220°C to obtain a convenient rate of reaction. The reaction temperature will depend on the particular aromatic polycarbamate being produced and should be below the temperature at which significant decomposition of the product might occur.

The process of the present invention is generally carried out at atmospheric pressure, although higher pressures of up to 50 bar may be used and especially at the higher reaction temperatures or when the reaction temperature is above the boiling point of the alcohol and/or reactant amine. Subatmospheric pressures may be employed, if desired.

The reaction between the urea, alcohol and the aromatic polyamine may be carried out in any suitable reactor, such as an autoclave, which is generally equipped with a means for agitation, means for regulating temperature and pressure and means for removing by-product ammonia, and possibly alcohol vapor. Although the order of addition of the reactants, and optional solvents and catalyst components may vary, a general procedure for carrying out the reaction is to charge the urea, aromatic polyamine, alcohol, inert solvent and catalyst if used into

the reaction vessel and then heat the mixture to the desired temperature at atmospheric pressure or higher pressures, if required. The reaction can be carried out batchwise, semicontinuous, or as a continuous process. The reaction products are recovered and treated by any conventional method, such as distillation or fractionation to effect separation of the aromatic polycarbamates from unreacted starting material, and optionally catalyst, solvent and by-products.

Ammonia resulting from the reaction must be removed during the course of the reaction, otherwise reduced yields of product carbamate are obtained. When the reaction is carried out at one atmosphere the ammonia is simply allowed to escape from the reaction vessel. In reactions where elevated pressures are employed provisions must be made to remove ammonia. A simple, convenient method is to strip the ammonia from the reactor with a dry inert gas, such as nitrogen and/or with the resulting alcohol vapor provided the alcohol employed is volatile at the reaction temperature. When the alcohol vapor is used to strip or aid in stripping the ammonia from the reactor, additional or makeup alcohol can be added to the reactor at a rate to compensate for the vapor loss.

The reaction time is generally dependent on the aromatic polycarbamate being produced, the reaction temperature and pressure, the solvent and the catalyst optionally employed and will vary depending on whether the process is continuous or batch. It will normally not exceed 5 hours. Reaction times of less than 4 hours are common, and reaction times of 3 hours have been achieved without any problem.

If the alcohol and the organic solvent are present in such ratio that an azeotropic mixture is formed, the subsequent removal of any alcohol is greatly facilitated.

The process of the present invention may be conducted batchwise or as a semi-continuous or continuous process.

The polycarbamates of this invention may be employed in a number of commercial applications, for example as chemical intermediates. They may be converted to the corresponding aromatic polyisocyanates and alcohols by thermal decomposition or other methods described in the prior art.

EXAMPLES

Example 1

2 g 4,4'-diaminodiphenylmethane diamine (DADPM), 3.6 g urea and 25 ml 1-methoxy-2-propanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 3 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 1-methoxy-2-propanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 93-97% yield of the bis(1-methoxy-2-propyl carbamate).

Example 2

6 g 4,4'-DADPM, 10.8 g urea and 25 ml 1-methoxy-2-propanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 3 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 1-methoxy-2-propanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 98% yield of the bis(1-methoxy-2-propyl carbamate) and 2% of the monocarbamate.

Example 3

2 g 4,4'-DADPM, 3.6 g urea and 25 ml 2-ethoxyethanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 3 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 2-ethoxyethanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 92-94% yield of the bis(2-ethoxyethyl carbamate).

Example 4

2 g 4,4'-DADPM, 2.43 g urea and 20 ml 2-methoxyethanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 2 hours. The alcohol was continuously added at a flow rate of 0.5

ml/min. and a mixture of ammonia and 2-ethoxyethanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 90% yield of the bis(2-methoxyethyl carbamate).

Example 5

2 g polyaminopolyphenylmethane (pDADPM), 2.43 g urea and 24 ml 1-methoxy-2-propanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 2 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 1-methoxy-2-propanol was continuously vented off, in such a rate that the reaction volume was kept constant. FTIR analysis showed a 92% yield of the polyphenylmethane polycarbamate.

Example 6

2 g pDADPM, 2.43 g urea and 24 ml 2-ethoxyethanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 2 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 2-ethoxyethanol was continuously vented off, in such a rate that the reaction volume was kept constant. FTIR analysis showed a 90% yield of the bis(2-ethoxyethyl carbamate).

Example 7

2 g 4,4'-DADPM, 2.43 g urea and 20 ml 2-methoxyethanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 2 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 2-ethoxyethanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 90% yield of the bis(2-ethoxyethyl carbamate).

Comparative example 1

2 g 4,4'-DADPM, 3.6 g urea and 23 ml butanol were put together in a

reaction vessel. The reaction mixture was heated at 190°C during 3 hours. Butanol was continuously added at a flow rate of 2.0 ml/min. and a mixture of ammonia and butanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 81-85% yield of the bisbutyl carbamate.

Comparative example 2

2 g 4,4'-DADPM, 2.4 g urea and 25 ml methanol were put together in a reaction vessel. The reaction mixture was heated at 200°C and under a pressure of 35bar during 3 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 2-ethoxyethanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 0.2 yield of the bis(2-methyl carbamate).

CLAIMS

1. A process for the preparation of an aromatic polycarbamate which comprises reacting an aromatic polyamine, urea and an alcohol, characterised in that the alcohol is an alkoxyated monoalcohol.
2. A process according to claim 1 wherein the alkoxyated monoalcohol has the formula $\text{CHR}^1\text{-(CR}^2\text{R}^3\text{-O)}_x\text{R}^4$ wherein x is an integer between 1 and 250 and $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ each are independently H or $\text{C}_1\text{-C}_{10}$ hydrocarbon radicals.
3. A process according to claim 1 or 2 wherein x is 1.
4. A process according to any of the preceding claims wherein the aromatic polyamine is selected from the group consisting of diaminodiphenylmethanes, toluenediamines, polyaminopolyphenylmethanes or mixtures thereof.
5. A process according to any of the preceding claims wherein the molar ratio of aromatic polyamine to urea is from about 1:1.2 to 1:10.
6. A process according to claim 5 wherein the molar ratio is from about 1:1.2 to 1:5.
7. A process according to any of the preceding claims wherein the alcohol is selected from the group consisting of 2-methoxy ethanol, 2-ethoxyethanol, 2-isopropoxyethanol, 1-methoxy-2-propanol, or mixtures thereof.
8. A process according to any of the preceding claims wherein the reaction temperature is in the range of from about 150 to 220 °C.
9. A process according to any of the preceding claims wherein the solvent is monochlorobenzene, ortho-dichlorobenzene, or mixtures thereof.
10. A process according to any of claims 1-9 wherein the reaction is carried out in the absence of an inert solvent.
11. A process according to any of the preceding claims which is carried out in the absence of a catalyst.

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 July 2001 (05.07.2001)

PCT

(10) International Publication Number
WO 01/47870 A3

(51) International Patent Classification⁷: C07C 269/04,
271/28

& T Centre, Thane Works, PO Box 155, Thane Belapur
Road, Thane, Maharashtra 400601 (IN). BOSMAN, Joris
[BE/BE]; Wezelsbaantje 29B, B-2230 Herselt (BE).

(21) International Application Number: PCT/EP00/12889

(74) Agents: MOENS, Marnix, Karel, Christiane et al.; In-
tellectual Property Dept., Everslaan 45, B-3078 Everberg
(BE).

(22) International Filing Date:
18 December 2000 (18.12.2000)

(25) Filing Language: English

(81) Designated States (*national*): IN, US.

(26) Publication Language: English

(84) Designated States (*regional*): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).

(30) Priority Data:
961/BOM/99 27 December 1999 (27.12.1999) IN

Published:

— with international search report

(71) Applicant (*for all designated States except US*): HUNTS-
MAN INTERNATIONAL LLC [US/US]; 500 Huntsman
Way, Salt Lake City, UT 84108 (US).

(88) Date of publication of the international search report:
21 March 2002

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): MANDAL, Sisir,
Kumar [IN/BE]; Eburonenstraat 65/48, B-1000 Brussels
(BE); SAPRE, Nitin, Yashwant [IN/IN]; ICI India R

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*



WO 01/47870 A3

(54) Title: PROCESS FOR THE PRODUCTION OF AROMATIC POLYCARBAMATES

(57) Abstract: A process for the preparation of an aromatic polycarbamate which comprises reacting an aromatic polyamine, urea and an alcohol, characterised in that the alcohol is an alkoxylated monoalcohol.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C269/04 C07C271/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 027 940 A (BAYER AG) 6 May 1981 (1981-05-06) cited in the application example 37 claims ---	1-10
X	EP 0 066 231 A (BAYER AG) 8 December 1982 (1982-12-08) examples 12,13 claims ---	1-11
A	US 5 453 536 A (DAI SHENGHONG A ET AL) 26 September 1995 (1995-09-26) cited in the application claims --- -/-	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *8* document member of the same patent family

Date of the actual completion of the international search

28 August 2001

Date of mailing of the international search report

05/09/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Pauwels, G

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 713 476 A (MERGER FRANZ ET AL) 15 December 1987 (1987-12-15) cited in the application example 11 -----	1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0027940 A	06-05-1981	DE 2943481 A	07-05-1981
		AT 4640 T	15-09-1983
		AU 538535 B	16-08-1984
		AU 6371380 A	30-04-1981
		BR 8006849 A	28-04-1981
		CA 1144562 A	12-04-1983
		DE 3064837 D	20-10-1983
		ES 496232 D	16-09-1981
		ES 8106883 A	01-12-1981
		JP 1652711 C	30-03-1992
		JP 3014819 B	27-02-1991
		JP 57114561 A	16-07-1982
		ZA 8006546 A	25-11-1981
EP 0066231 A	08-12-1982	DE 3122013 A	30-12-1982
		BR 8203231 A	17-05-1983
		CA 1182467 A	12-02-1985
		DE 3266154 D	17-10-1985
		ES 512786 D	01-03-1983
		ES 8304543 A	01-06-1983
		JP 1618641 C	30-09-1991
		JP 2045617 B	11-10-1990
		JP 57209263 A	22-12-1982
US 5453536 A	26-09-1995	DE 69511248 D	09-09-1999
		DE 69511248 T	02-12-1999
		EP 0749420 A	27-12-1996
		HU 76526 A	29-09-1997
		JP 9510705 T	28-10-1997
		WO 9524384 A	14-09-1995
US 4713476 A	15-12-1987	DE 2917493 A	13-11-1980
		AT 1945 T	15-12-1982
		BR 8002598 A	09-12-1980
		CA 1117968 A	09-02-1982
		DE 3061256 D	13-01-1983
		EP 0018586 A	12-11-1980
		JP 1015499 B	17-03-1989
		JP 1536846 C	21-12-1989
		JP 55145657 A	13-11-1980
		JP 1038055 A	08-02-1989
		JP 1627390 C	28-11-1991
		JP 2048539 B	25-10-1990
		US 4851565 A	25-07-1989
		ZA 8002579 A	24-06-1981

Form PCT/ISA/210 (patent family annex) (July 1992)